

888

The content enclosed with or attached to this notice has been reproduced from that publication by permission of the copyright owner. It may not be further reproduced or publicly displayed without express permission of the copyright owner. Any unauthorized reproduction or use may subject you to financial and other penalties.

R dpmorris@us.ibm.com/--354936 Daniel P. Morris

Copies: **1**

ORDER ARKIV FOER KEMI VOL 5

AUTHOR Aurivillus, B.,

AGE 39-EOA

BY

YEAR 1952

ISSN 03656128

ODEN BLK_02/17/05_0365-6128_307395

CHECKSUM 00090130048007110

ILLING 888

SERVICE REGULAR

INF. # BESG090130048-1

CONTACT Alma Gardner almag@us.ibm.com Phone 914-642-6811 Fax 914-642-6820

COMMENT

**FAX*****dpmorris@us.ibm.com****888**Alma Gardner
IBM InfoGate

LH, SU

Dept. 40L, L/2C908, MD/238
1133 Westchester Avenue
White Plains, NY 10604
USA

February 17, 2005



0E YVO939

888 T 3472

For questions about this order contact us at orderhelp@ieonline.com.**BEST AVAILABLE COPY**

Best Available Copy

ARKIV FÖR KEMI Band 5 nr 4

Communicated 14 May 1952 by ARNE WRSTGREN

The structure of $\text{Bi}_2\text{NbO}_5\text{F}$ and isomorphous compounds

By BENGT AURIVILLIUS

With 1 figure in the text

X-ray studies made previously on the compounds $\text{CaBi}_2\text{Nb}_2\text{O}_9$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (1) showed that they have very similar structures. The symmetry is tetragonal or pseudotetragonal, and the structures are each built up of quadratic Bi_2O_3 layers alternating with perovskite layers, the latter having different heights in the three different cases. The generalized formula for the compounds might be written $Me'_2\text{O}_3$ ($Me'_{m-1} R_m \text{O}_{8m+1}$) where Me' is the 12 coordinated metal atom in the perovskite layers and R the 6 coordinated atom. The formulae for the above compounds, $\text{Bi}_2\text{O}_3(\text{CaNb}_2\text{O}_7)$, $\text{Bi}_2\text{O}_3(\text{Bi}_2\text{Ti}_3\text{O}_{10})$ and $\text{Bi}_2\text{O}_3[(\text{BaBi}_2)_2\text{Ti}_4\text{O}_{13}]$ thus have m values of 2, 3 and 4. The simplest case, $m=1$, would correspond to the formula $Me'_2\text{O}_3(\text{RO}_4)$ and to a structure built up of $Me'_2\text{O}_3$ layers and layers of RO_6 octahedra each octahedron sharing four corners. Compounds of this type have, however, not been successfully synthesized as yet.

The present paper deals with the compounds $\text{Bi}_2\text{NbO}_5\text{F}$, $\text{Bi}_2\text{TaO}_5\text{F}$ and $\text{Bi}_2\text{TiO}_4\text{F}_2$, which correspond to the simplest case, $m=1$ above, except that some of the O atoms are replaced by F atoms. The formulae of the compounds might thus be written: $\text{Bi}_2(\text{O}, \text{F})_2\text{Nb}(\text{O}, \text{F})_4$ etc.

Preparation, powder photographs and analyses

$\text{Bi}_2\text{NbO}_5\text{F}$: When a mixture of BiF_3 and Nb_2O_5 in the mol ratio 4:1 was heated in air at 800°C for a short time, a few single crystals (very thin plates) were obtained. Powder photographs of this sample indicated a tetragonal unit cell with the same cell dimensions as would be expected for the above general type when $m=1$. The best conditions for the formation of this phase were then studied by heating 2.5 g mixtures ($2\text{BiF}_3 + \frac{1}{2}\text{Nb}_2\text{O}_5$) in air at 640°C , this low temperature being chosen to reduce the volatility of the BiF_3 . The reaction times were varied from 5–40 hours, and powder photographs were taken of each product. For reaction times of 7–15 hours the lines of the above tetragonal phase predominated in the powder photographs, the few extra lines were very weak (see Table 1).

The fluorine content was found to vary from 4.0 % (7 hours) to 2.4 % (15 hours), whereas the calculated value for $\text{Bi}_2\text{NbO}_5\text{F}$ is 3.2 %. No variation in the size of the cell with the fluorine content was found, and it therefore seems probable that the composition of the phase is constant and that the observed variation in the F content is due to the presence of small impurities which are not visible in the powder photo-

Best Available Copy

B. AURIVILLIUS, *The structure of $\text{Bi}_2\text{NbO}_5\text{F}$ and isomorphous compounds*

Table I
Powder photographs of $\text{Bi}_2\text{NbO}_5\text{F}$ (sample with 2.8 % F)
Or K radiation $\lambda_{C, K_d} = 2.2909 \text{ \AA}$

| $h k l$ | $10^4 \cdot \sin^2 \theta_{\text{calc}}$ | $10^4 \cdot \sin^2 \theta_{\text{obs}}$ | I_{obs} |
|----------|--|---|------------------|
| 1 0 3 | 1319 | 1332 | |
| 0 0 6 | 1708 | 1711 | st |
| 1 1 0 | 1784 | 1795 | m |
| 1 1 2 | 1974 | 1969 | m |
| 1 0 5 | 2078 | 2083 | vvw |
| 1 1 4 | 2543 | 2547 | m |
| — | — | 2785 | vvw |
| 0 0 8 | 3036 | 3033 | w |
| — | — | 3093 | vw |
| 1 1 6 | 3492 | 3490 | st |
| 2 0 0 | 3568 | 3567 | st |
| 2 0 2 | 3758 | 3754 | vw |
| — | — | 3808 | vw |
| { 1 0 9 | 4734 } | 4737 | st |
| { 0 0 10 | 4743 } | 4737 | st |
| 1 1 8 | 4820 | 4827 | w |
| 2 1 3 | 4888 | 4891 | st |
| 2 0 6 | 5276 | 5292 | m |
| 2 1 5 | 5647 | 5658 | w |
| 1 1 10 | 6527 | 6529 | vw |
| 1 0 11 | 6631 | 6630 | w |
| 0 0 12 | 6830 | 6841 | w |
| 2 2 0 | 7137 | 7139 | w |
| 2 2 2 | 7327 | 7330 | vw |
| 3 0 1 | 8076 | 8080 | vvw |
| { 2 1 9 | 8303 } | 8304 | st |
| { 2 0 10 | 8311 } | 8304 | st |
| 3 0 3 | 8456 | 8456 | m |
| 1 1 12 | 8614 | 8611 | m |
| 2 2 6 | 8845 | 8844 | m |
| { 1 0 13 | 8908 } | 8919 | m |
| { 3 1 0 | 8921 } | 9119 | vw |
| 3 1 2 | 9111 | 9119 | vw |
| 3 0 5 | 9215 | 9195 | vw |
| 0 0 14 | 9297 | 9292 | vw |

graphs. To check that the Bi/Nb ratio had not changed essentially during the heating, a complete analysis was made on one sample (9 hours heating). The following values were obtained as the mean of three analyses: Bi: $68.0 \pm 0.6\%$, Nb: $14.2 \pm 0.6\%$, F: $3.7 \pm 0.2\%$.

The values calculated for $\text{Bi}_2\text{NbO}_5\text{F}$ are:

Bi: 68.5, Nb: 15.2 %, F: 3.2 %.

From these figures it seems probable that the formula of the compound is $\text{Bi}_2\text{NbO}_5\text{F}$.

$\text{Bi}_2\text{TaO}_5\text{F}$ was prepared in exactly the same way as $\text{Bi}_2\text{NbO}_5\text{F}$. No analysis was made since the powder photographs were similar to those of $\text{Bi}_2\text{NbO}_5\text{F}$ and niobium and tantalum compounds are usually isomorphous.

Fig. 1. C

Bi_2TiO_4
2:1 (total
photogra
assuming
the same
phase are
of the mi
variation
are 7.8 %
fluorine a
of Bi_2Nb
 $\text{Bi}_2\text{TiO}_4\text{F}_2$

Method
with NaOJ
(3). The di

Bismut
was deterr
precipitate
as such.

The dim
with focusi

ARKIV FÖR KEMI. Bd 5 nr 4

Best Available Copy

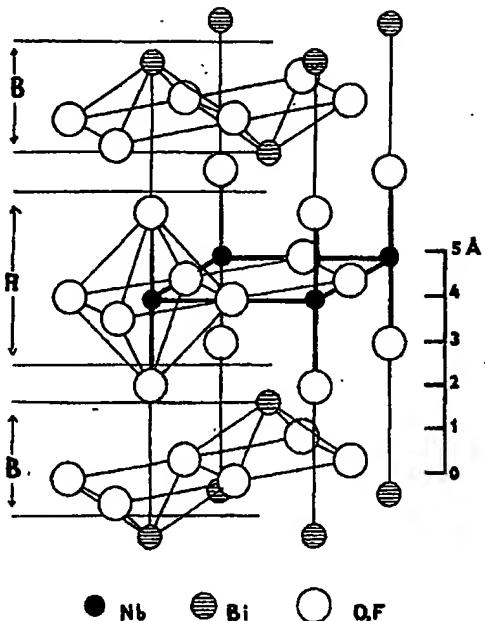


Fig. 1. One half of the unit cell of $\text{Bi}_2\text{NbO}_5\text{F}$. A denotes the region of $\text{Nb}(\text{O}, \text{F})_6$ octahedra and B the $\text{Bi}_2(\text{O}, \text{F})_2$ layers.

$\text{Bi}_2\text{TiO}_4\text{F}_2$: Mixtures of bismuth fluoride and titanium oxide in the mol ratio 2:1 (total 2.3 g) were heated in air at 640° for various lengths of time. The powder photographs obtained from samples heated for 3 or 5 hours could be interpreted by assuming a mixture of BiOF (2) and a phase whose cell dimensions were nearly the same as those of $\text{Bi}_2\text{NbO}_5\text{F}$. (See Table 2, where the reflexions from the BiOF phase are designated by b and those from the other phase by a). The fluorine contents of the mixed samples were found to be 6.4% (5 hours) and 8.4% (3 hours) but no variation of the cell size with the fluorine content was found. The calculated values are 7.8% for BiOF and 6.7% for $\text{Bi}_2\text{TiO}_4\text{F}_2$. From the original Bi/Ti ratio, from the fluorine analysis and from the similarity of the powder photographs with those of $\text{Bi}_2\text{NbO}_5\text{F}$ (Tables 1 and 2), it was concluded that the formula of the phase is $\text{Bi}_2\text{TiO}_4\text{F}_2$.

the heating, owing values
 $2 \pm 0.6\%$, F:

Methods of analysis: Fluorine. The samples were first decomposed by fusing with NaOH , and were then distilled with HClO_4 as described by WILLARD and WINTER (3). The distillate was titrated with $\text{Th}(\text{NO}_3)_4$ using Na-alizarinsulphonate as indicator.

Bismuth and Niobium. The samples were brought into solution, and niobium was determined as described in Scott's "Standard Methods" (4). Bismuth was first precipitated as Bi_2S_3 , which was then redissolved, converted to Bi_2O_3 and weighed as such.

s $\text{Bi}_2\text{NbO}_5\text{F}$.

No analysis
 NbO_5F and

Unit cells and space group

The dimensions of the unit cells were determined from powder photographs taken with focusing cameras of the Phragmén type (Tables 1 and 2). The radiation used

Best Available Copy

B. AURIVILLIUS, *The structure of Bi_2NbO_5F and isomorphous compounds*

Table 2

Powder photographs of $Bi_2TiO_4F_2$ (mixed with $BiOF$) $Cr K$ radiation
 $(\lambda_{Cr K_\alpha} = 2.2909 \text{ \AA})$. a denotes the $Bi_2TiO_4F_2$ phase and b the $BiOF$ phase

| $h k l$ | phase | $10^4 \sin^2 \theta_{\text{calo}}$ | $10^4 \sin^2 \theta_{\text{obs}}$ | I_{obs} |
|----------|-------|------------------------------------|-----------------------------------|------------------|
| 1 0 1 | a | 957 | 941 | |
| 1 0 1 | b | 1270 | 1266 | m |
| { 1 0 3 | a | 1351 } | | |
| { 0 0 2 | b | 1352 } | 1354 | st |
| 0 0 6 | a | 1771 | 1787 | m |
| 1 1 0 | a | 1818 | 1811 | m |
| 1 1 0 | b | 1864 | 1858 | m |
| 1 1 2 | a | 2013 | 1999 | vvv |
| 1 0 5 | a | 2138 | 2132 | w+ |
| 1 0 2 | b | 2284 | 2288 | vvv |
| 1 1 4 | a | 2603 | 2601 | m |
| - | - | - | 3074 | vw |
| 1 1 2 | b | 3216 | 3231 | w |
| 1 0 7 | a | 3319 | 3320 | vw |
| 1 1 6 | a | 3587 | 3600 | st |
| 2 0 0 | a | 3631 | 3624 | st |
| 2 0 0 | b | 3728 | 3744 | w |
| 2 0 2 | a | 3828 | 3822 | w |
| 1 0 3 | b | 3974 | 3982 | w |
| - | - | - | 4352 | vvv |
| 2 0 4 | a | 4418 | 4426 | vvv |
| 2 1 1 | a | 4588 | 4590 | w |
| - | - | - | 4674 | vvv |
| { 1 0 9 | a | 4893 } | | |
| { 1 1 3 | b | 4906 } | | |
| { 0 0 10 | a | 4919 } | 4904 | st |
| 2 1 3 | a | 4982 | 4979 | st |
| 2 0 2 | b | 5080 | 5084 | w |
| { 2 0 6 | a | 5402 } | | |
| { 0 0 4 | b | 5408 } | 5416 | m+ |
| 2 1 5 | a | 5789 | 5788 | m |
| 2 1 2 | b | 6012 | 6025 | m |
| 1 0 4 | b | 6340 | 6353 | w |
| { 2 0 3 | b | 6770 } | | |
| { 2 0 8 | a | 6779 } | 6786 | m |
| 1 0 11 | a | 6860 | 6869 | m |
| 2 1 7 | a | 6950 | 6950 | vvv |
| 0 0 12 | a | 7084 | 7075 | m |
| { 2 2 0 | a | 7262 } | | |
| { 2 1 4 | b | 7272 } | 7262 | m |
| { 2 2 0 | b | 7455 } | | |
| { 2 2 2 | a | 7459 } | 7456 | w |
| 2 1 3 | b | 7702 | 7709 | m |
| - | - | - | 8049 | vw |
| 3 0 1 | a | 8210 | 8210 | vw |
| - | - | - | 8352 | vw |
| { 2 1 9 | a | 8524 } | | |
| { 2 0 10 | a | 8550 } | 8524 | st |
| 3 0 3 | a | 8613 | 8603 | m |
| 3 0 1 | b | 8736 | 8725 | w |
| 2 2 2 | b | 8814 | 8807 | w |
| 1 1 12 | a | 8900 | 8900 | m |

was t
be int

The
The
agrees
calcul:
Zero
was n:
than 1
 $h+k+$
Pow
and frc

Bi_2N
unit ce
the ma:
for l od
the Pat
sity val
here) sh
of other
position
or 0 0 0.
gave th:
No de
For B
meter. A
occupy t
was obt:

ARKIV FÖR KEMI. Bd 5 nr 4

Table 2 (continued)

| <i>h k l</i> | phase | $10^4 \sin^2 \theta_{\text{calc}}$ | $10^4 \sin^2 \theta_{\text{obs}}$ | I_{obs} |
|--------------|----------|------------------------------------|-----------------------------------|------------------|
| 2 2 6 | <i>a</i> | 9033 | 9027 | m |
| 3 1 0 | <i>a</i> | 9078 | 9072 | w |
| 2 0 4 | <i>b</i> | 9136 | 9136 | vw |
| 3 1 2 | <i>a</i> | 9275 | 9272 | m |
| 3 1 0 | <i>b</i> | 9319 | 9319 | w |
| { 1 0 5 | <i>b</i> | 9382 } | 9384 | m |
| { 3 0 5 | <i>a</i> | 9400 } | | |

was CrK ($\lambda_{CrK} = 2.2909 \text{ \AA}$). As mentioned above the powder photographs could be interpreted by assuming tetragonal unit cells; the cell dimensions are given below.

| | <i>a</i> (\text{\AA}) | <i>c</i> (\text{\AA}) |
|----------------------|-----------------------|-----------------------|
| Bi_2NbO_5F | 3.835 | 16.63 |
| Bi_2TaO_5F | 3.829 | 16.64 |
| $Bi_2TiO_4F_2$ | 3.802 | 16.33 |

The errors in these figures are estimated to be $\pm 0.1 \%$.

The observed density was 8.0 for Bi_2NbO_5F (preparation with 2.8% F), which agrees fairly well with the assumption of 2 formula units per unit cell, giving a calculated density of 8.26.

Zero and first order Weissenberg photographs around the *a* axis were taken. There was nothing in the Weissenberg photographs to indicate a Laue symmetry lower than D_{4h} —4/mmm. The only extinctions found were that *h*, *k*, *l* were absent for *h+k+l* odd, which is characteristic of the space groups C_{4h}^6 , D_{2d}^6 , D_{2d}^{11} and D_{4h}^{17} .

Powder photographs only were taken of the compounds Bi_2TaO_5F and $Bi_2TiO_4F_2$, and from these it was concluded that these substances are isomorphous with Bi_2NbO_5F .

Positions of the metal atoms

Bi_2NbO_5F : With 2 formula units per unit cell there are 4 Bi and 2 Nb atoms per unit cell. The intensities of the spots in the Weissenberg photographs seemed in the main to depend only on the *l* values. Thus for *l* even $I_{00l} \approx I_{11l} \approx I_{20l}$ etc. and for *l* odd: $I_{10l} \approx I_{21l} \approx I_{30l}$ etc. With these intensity values a good approximation of the Patterson-Harker function along 00z could be obtained by using only the intensity values of $h0l$ and $h1l$. The Patterson-Harker function thus calculated (not given here) showed only one, big, maximum, at $z=0.34$. This maximum, and the absence of others, could be explained only by assuming that 4 Bi atoms are situated at the positions $\pm 00z$ with $z=0.17$ or $z=0.33$, and the Nb atoms at the positions $00\frac{1}{2}$ or 000 . Arbitrarily choosing 000 as the position for Nb; trial and error calculations gave the value 0.325 for the Bi parameter.

No determination of z_{Bi} was made for Bi_2TaO_5F .

For $Bi_2TiO_4F_2$ the powder photograph data were used to determine the Bi parameter. Assuming the Ti atoms to be situated at 000 and the O and the F atoms to occupy the same positions as given below for Bi_2NbO_5F , the value $z_{Bi}=0.327 \pm 0.006$ was obtained from trial and error calculations.

B. AURIVILLIUS, *The structure of $\text{Bi}_2\text{NbO}_5\text{F}$ and isomorphous compounds*

Best Available Copy

Table 3
Weissenberg photographs of $\text{Bi}_2\text{NbO}_5\text{F}$

Zero layer

| | $h k$ | 0 0 | | 2 0 | | 4 0 | | |
|--------|-------|-------------------|------------------|-------------------|------------------|-------------------|------------------|--------|
| | | I_{calc} | I_{obs} | I_{calc} | I_{obs} | I_{calc} | I_{obs} | |
| l 0 | | — | — | 170 | vst | 37 | w | l 0 |
| 2 | | — | — | 10 | w | 3 | vw | 2 |
| 4 | | 0.3 | — | 0.04 | — | 0.05 | — | 4 |
| 6 | | 220 | vst | 67 | w | 34 | vw | 6 |
| 8 | | 12 | w | 5 | vw | 6 | vvw | 8 |
| 10 | | 3 | vw | 2 | — | 2 | — | 10 |
| 12 | | 44 | st | 26 | w | 86 | st | 12 |
| 14 | | 15 | m | 11 | w | | | 14 |
| 16 | | 10 | w | 10 | w | | | 16 |
| 18 | | 16 | m | 28 | m | | | 18 |
| 20 | | 22 | m | | | | | 20 |
| | $h k$ | 1 0 | | 3 0 | | | | |
| l 1 | | I_{calc} | I_{obs} | I_{calc} | I_{obs} | l 1 | | l 1 |
| 3 | | 7 | w | 1 | vw | 3 | | 3 |
| 5 | | 270 | vst | 42 | w | 5 | | 5 |
| 7 | | 40 | w | 8 | vw | 7 | | 7 |
| 9 | | 1 | — | 0.2 | — | | | 9 |
| | | 75 | m | 30 | vw | | | 11 |
| 11 | | 18 | w | 10 | vw | | | 11 |
| 13 | | 3 | vw | 3 | vw | | | 13 |
| 15 | | 20 | m | 19 | m | | | 15 |
| 17 | | 12 | w | | | | | 17 |
| 19 | | 14 | w | | | | | 19 |

Positions of the O and the F atoms

The positions of the O and the F atoms could not be distinguished either from the diffraction data, or from space considerations because of the similarity in the reflecting power and ionic radii of O^{2-} and F^- . The problem is therefore treated as though O and F were the same atomic species. In the following, the O and the F atoms are denoted by (O, F) and the discussion relates to $\text{Bi}_2\text{NbO}_5\text{F}$ for which z_{Bi} could be accurately determined from the Weissenberg photographs.

It seemed reasonable to assume that the Nb atoms are surrounded by a regular or nearly regular octahedron of (O, F) atoms with distances $\text{Nb}-(\text{O}, \text{F}) \approx 2.0 \text{ \AA}$. Neglecting the polar space group C_{4v}^0 , these conditions are fulfilled only if 4 (O, F) atoms, here called (O, F)₁, are situated at the positions $\pm 0z$ with $z \approx 0.12$, and 4 (O, F) atoms, (O, F)₂, at the positions $0 \pm 0, \pm 00$. Assuming the distance (O, F)-(O, F) to be $\geq 2.5 \text{ \AA}$ and the distance Bi-(O, F) to be $\geq 2.2 \text{ \AA}$ there is only room for the remaining 4 (O, F) atoms, (O, F)₃, at the positions $0 \pm \frac{1}{2}, \pm 0 \frac{1}{2}$.

The co-

The pro-
ties for t
derived asThe line
indicated t
the agree

ARKIV FÖR KEMI. Bd 5 nr 4

Table
photographs of NbO_5F $\text{Cu K}\alpha$ radiation

First layer

| 4 0 | | <i>h k</i> | 1 1 | | 3 1 | | |
|--------------------------|-------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------|
| <i>I</i> _{calc} | <i>I</i> _{obs} | <i>l</i> | <i>I</i> _{calc} | <i>I</i> _{obs} | <i>I</i> _{calc} | <i>I</i> _{obs} | |
| 37 | w | 0 | 210 | vst | 36 | w | |
| 3 | vw | 2 | 17 | w | 4 | vvw | |
| 0.05 | — | 4 | 11 | w | 2 | — | |
| 34 | vw | 6 | 110 | m | 33 | w | |
| 6 | vvw | 8 | 27 | vw | 9 | vw | |
| | | | | | | | |
| 2 | — | 10 | 2 | vvw | 1 | — | |
| | | 12 | 21 | m | 20 | w | |
| 86 | st | 14 | 14 | w | 20 | w | |
| | | 16 | 5 | w | 17 | w | |
| | | 18 | 19 | m | | | |
| | | 20 | 58 | st | | | |
| h k | | 0 1 | 2 1 | | 4 1 | | |
| <i>l</i> | | <i>I</i> _{calc} | <i>I</i> _{obs} | <i>I</i> _{calc} | <i>I</i> _{obs} | <i>I</i> _{calc} | <i>I</i> _{obs} |
| 1 | | 7 | — | 2 | vw | 1 | vvw |
| 3 | | 270 | vst | 74 | m | 33 | w |
| 5 | | 40 | m | 13 | w | 7 | — |
| 7 | | 1 | — | 0.3 | — | 0.2 | — |
| | | | | | | | |
| 9 | | 75 | vst | 40 | w | 53 | w |
| 11 | | 18 | m | 12 | vvw | 51 | w |
| | | | | | | | |
| 13 | | 3 | vw | 3 | vw | | |
| 15 | | 20 | m | 19 | m | | |
| 17 | | 12 | w | 19 | m | | |
| 19 | | 14 | w | | | | |

The coordination and distances in Å will be:

$$\text{Bi}-4(\text{O}, \text{F})_3 = 2.29 \quad \text{Nb}-2(\text{O}, \text{F})_1 = 2.0$$

$$\text{Bi}-4(\text{O}, \text{F})_1 = 2.9 \quad \text{Nb}-4(\text{O}, \text{F})_2 = 1.92$$

$$(\text{O}, \text{F})_3-4(\text{O}, \text{F})_3 = 2.71 \quad (\text{O}, \text{F})_2-4(\text{O}, \text{F})_2 = 2.71$$

$$(\text{O}, \text{F})_1-4(\text{O}, \text{F})_3 = 2.9 \quad (\text{O}, \text{F})_1-4(\text{O}, \text{F})_2 = 2.8$$

The proposed structure is given in the summary. Calculated and observed intensities for the reflexions in the Weissenberg photographs are given in Table 3. I_{calc} is derived as follows:

$$I_{\text{calc}} = \frac{1 + \cos^2 2\theta}{1600 \cdot \sin 2\theta} \cdot F^2 \text{ where } F = \sum f \cos 2\pi(hx + ky + lz).$$

The lines of maximum absorption in the Weissenberg photographs (see 5) are indicated by dotted lines in Table 3. If the absorption effects are taken into account, the agreement between calculated and observed intensities is quite good.

Best Available Copy

either from the
arity in the re-
fore treated as
ne O and the F
F for which z_{Bi}

ed by a regular
 $(\text{O}, \text{F}) \approx 2.0 \text{ \AA}$
only if $4(\text{O}, \text{F})$
th $z \approx 0.12$, and
distance (O, F)
is only room for

Best Available Copy

B. AURIVILLIUS, *The structure of $\text{Bi}_2\text{NbO}_5\text{F}$ and isomorphous compounds*

Discussion of the structure

Even if the $(\text{O}, \text{F})_1$ atoms (see above) are assumed to occupy such a position that the distance $\text{Bi}-4(\text{O}, \text{F})_1$ is as small as possible [$z(\text{O}, \text{F})_1 = 0.15$, $(\text{O}, \text{F})_1 - (\text{O}, \text{F})_3 = 2.5$, $\text{Nb}-2(\text{O}, \text{F})_1 = 2.5$, $\text{Bi}-4(\text{O}, \text{F})_1 = 2.7$], the distance $\text{Bi}-4(\text{O}, \text{F})_1$ will still be much longer than the distance $\text{Bi}-4(\text{O}, \text{F})_3$. It therefore seems appropriate to describe the structure of $\text{Bi}_2\text{NbO}_5\text{F}$ as being built up of $\text{Bi}_2(\text{O}, \text{F})_2$ layers alternating with octahedral layers having the composition $\text{Nb}(\text{O}, \text{F})_4$, both layers being perpendicular to the c -axis. It might be pointed out that the structure of $\text{Bi}_2(\text{O}, \text{F})_2\text{Nb}(\text{O}, \text{F})_4$ is basically of the same type as the " X_1 structures", $M\text{e}_2\text{O}_2X$, previously investigated by SILLÉN (6). Thus the octahedral sheets $\text{Nb}(\text{O}, \text{F})_4$ correspond to single layers of halogen atoms, X , in $M\text{e}_2\text{O}_2X$.

Discussion of the distribution of the O and the F atoms

As seen above, the distance $\text{Bi}-4(\text{O}, \text{F})_3$ is 2.29 Å for $\text{Bi}_2\text{NbO}_5\text{F}$. For $\text{Bi}_2\text{TiO}_4\text{F}$, the corresponding distance is calculated to be 2.26 ± 0.06 Å. These distances are very nearly the same as the corresponding distances, $\text{Bi}-4\text{O}$, within the Bi_2O_3 layers of other bismuth oxides (6). This need not, however, necessarily mean that the $\text{Bi}_2(\text{O}, \text{F})_2$ layers (see the figure) are free from F atoms, since compounds with $\text{Bi}_2(\text{O}, \text{F})_2$ layers which certainly contain F atoms have not been investigated hitherto, and thus the distances within such layers are unknown.

For the present it seems therefore best to make no special assumptions as to the distribution of the O and F atoms.

SUMMARY

The crystal structure of $\text{Bi}_2\text{NbO}_5\text{F}$ has been investigated by means of Weissenberg and powder photographs. From powder photographs the compounds $\text{Bi}_2\text{TaO}_5\text{F}$ and $\text{Bi}_2\text{TiO}_4\text{F}_2$ have been found to be isomorphous with $\text{Bi}_2\text{NbO}_5\text{F}$. The following structure is proposed for $\text{Bi}_2\text{NbO}_5\text{F}$:

| $D_{4h}^{17}-I\bar{4}/mmm$ | | |
|--|----------|--|
| $(000, \frac{1}{2}\frac{1}{2}\frac{1}{2}) +$ | | |
| 2 Nb | in 2 (a) | : 000 |
| 4 Bi | in 4 (e) | : $\pm 00z$ $z = 0.325 \pm 0.001$ |
| 4 (O, F) ₁ | in 4 (e) | : $0\frac{1}{2}0, \frac{1}{2}00$ |
| 4 (O, F) ₂ | in 4 (e) | : $\pm 00z$ $z = 0.12 \pm 0.01$ |
| 4 (O, F) ₃ | in 4 (d) | : $0\frac{1}{2}t, \frac{1}{2}0\frac{1}{2}$ |

The cell dimensions are $a = 3.835$ Å, $c = 16.63$ Å for $\text{Bi}_2\text{NbO}_5\text{F}$. The positions of the metal atoms were determined from the diffraction data, those of the (O, F) atoms from space considerations. Although it does not seem improbable that O atoms alone occupy the positions $0\frac{1}{2}t, \frac{1}{2}0\frac{1}{2}$, Bi and O thus forming Bi_2O_3 layers as in other bismuth oxides, nothing can be definitely stated as to the distribution of the O and F atoms.

The structure is built up of quadratic $\text{Bi}_2(\text{O}, \text{F})_2$ layers alternating with octahedral sheets having the composition $\text{Nb}(\text{O}, \text{F})_4$ (see figure) and the formula might thus be written: $\text{Bi}_2(\text{O}, \text{F})_2\text{Nb}(\text{O}, \text{F})_4$. The structure is formally related to a series of

previo
represe

Univ

REF.
Mineral.
Ed. 5 (1
edited b
(1937) 4

ds

ARKIV FÖR KEMI. Bd 5 nr 4

previously investigated structures of general formula Me_2O_3 ($Me_{m-1}R_mO_{3m+1}$) and represents the simplest case of this series, i.e. $m=1$.

University of Stockholm, Institute of Inorganic and Physical Chemistry, May 1952.

REFERENCES. 1. Aurivillius, B., Arkiv Kemi 2 (1950) 519. — 2. —, Arkiv Kemi Mineral. Geol., 26 B (1948) no 2. — 3. Willard, H. H. and Winter, O. B., Ind. Eng. Chem. Anal. Ed. 5 (1933) 7. — 4. Standard Methods of Chemical Analysis by W. W. Scott, fifth edition, edited by N. H. Furman, New York 1925, p. 335 and p. 338. — 5. Wells, A. F., Z. Krist. 96 (1937) 451. — 6. Sillén, L. G., Dissert. Stockholm 1940.

such a position
 $=0.15$, $(O, F)_1$
 $Bi-4 (O, F)_1$ will
 before seems ap-
 prop of $Bi_2(O, F)_2$
 $Nb (O, F)_4$, both
 at the structure
 tures", Me_2O_3X ,
 $(O, F)_4$ correspond

.toms.

For Bi_2TiO_4F ,
 se distances are
 ithin the Bi_2O_3
 necessarily mean
 nce compounds
 en investigated

ptions as to the

of Weissenberg
 Bi_2TaO_5F and
 following struc-

The positions of
 e of the (O, F)
 ple that O atoms
 Bi_2O_3 layers as
 to the distribu-

with octahedral
 nula might thus
 l to a series of

Best Available Copy

Tryckt den 24 november 1952

Uppsala 1952. Almqvist & Wiksell Boktryckeri AB